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Patentanmeldung Nr. Patent application No. Demande de brevet n°

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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

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Method for making thin film devices intended for solar cells or SOI application

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METHOD FOR MAKING THIN FILM DEVICES INTENDED FOR SOLAR CELLS OR SOI APPLICATIONS

Field of the invention

[0001] The present invention is related to micro-electronics and more particular to the field of thin film device applications such as silicon-on-insulator (SOI) structures or solar cells in particular. Furthermore, the present invention is relating to a manufacturing method of such devices.

State of the art

[0002] The silicon wafers found in existing semiconductor devices usually have a thickness of several hundred microns. However, the electrically active domain of a wafer is limited to its surface, in fact, less than a few microns of thickness is needed. The remained part of a wafer is used as substrate. Unfortunately, this excess of material causes both a rise in power consumption and a fall in the operating speed of the device. The SOI wafers incorporate an insulating layer between its very thin (less than a few microns) active domain and its much thicker substrate. The substrate is isolated and can thus no longer deteriorate the speed or efficiency of the active layer.

[0003] Silicon on insulator technology (SOI) involves the formation of a monocrystalline silicon semi-conductor layer on an insulating material such as silicon oxide.

[0004] One important application of a thin film device is the manufacturing of solar cells. Solar cells usually comprise on the top of a silicon wafer an active surface in the form of a thin film device deposited on said silicon wafer.

[0005] During the conversion of light into electrical energy, as mentioned above, only the top few microns of said top layer are really active. The major part of this silicon wafer only provides mechanical strength to the device. This function can be achieved by any other low-cost substrate compatible to the production process. The requirements for such a substrate, excepted low cost, are high temperature stability (1100°C), matching of the thermal expansion coefficients and low impurity contents.

[0006] More generally, in the prior art, the preparation of a porous semiconductor layer on a substrate as a sacrificial layer for solar cell usually comprises several steps such as at least a porous semiconductor layer formation on an original substrate, epitaxial silicon layer deposition, device fabrication on said substrate and separation of the device from the original substrate and transfer to a foreign substrate in order to possibly re-use the original substrate. This sequence is largely illustrated in the documents US-B- 6 258 698 (Iwasaki et al, Canon), US-B- 6 211 038 (Nakagawa et al, Canon) and US-B- 6 326 280 (Tayanaka, Sony Corporation).

[0007] In the prior art, several methods are known to separate thin (porous) semiconductor films from a substrate. All those methods use a lift-off or peeling-off process at the end of the production chain. The drawback of these methods is that during all the process steps, parameters such as temperature, pressure and chemicals are conditioned by the resistance of the original substrate. The film separation and its transfer is the last

technological step that requires to preserve the high-porous characteristics of the Si layer. The fact of maintaining said porous characteristics throughout many high-temperature steps allows only a narrow processing window in terms of process temperature and porosity. Moreover in said case, the transfer is difficult to achieve properly.

[0008] In particular, a lift-off process is described in EP-A-1132952 where it is shown that a thin porous silicon film of 5 to 50 μm can be separated from the silicon substrate whereon it is deposited. In such case, the substrate can be re-used many times for getting new porous silicon films. Other possible techniques for thin film separation are ion implantation or wafer bonding techniques.

Aims of the invention

[0009] The present invention aims to provide a method for the preparation of thin-film devices for structures being highly efficient and low-cost. Examples of such structures are silicon-on-insulator (SOI) structures or solar cells. The use of thin film in SOI structures in general and in solar cells in particular allows the reduction of the amount of material consumed per structure, which significantly reduces the high costs of the active substrate, while the quality of the film provides the good characteristics of the whole device.

Summary of the invention

[0010] The present invention relates to a method for manufacturing a semiconductor device, said method comprising at least the following subsequent steps:

(a) formation of a porous semiconductor layer in the form of a thin film on an original substrate, said formation being immediately followed by the step of

(b) separation of said thin film by a lift-off process from said original substrate;

(c) fabrication of a device on said thin film;

(d) transfer and attachment of said device on a foreign substrate.

[0011] According to a preferred embodiment of the present invention, the step of the fabrication of the device comprises the transfer of said thin film to a dummy support whereon the deposition of an active semiconductor layer is performed on said thin film, optionally followed by the fabrication of a contacted device on said active semiconductor layer.

[0012] Furthermore, the lift-off process according to the present invention is achieved by immersing the substrate in a HF solution in concentration between 12 and 35% and using current densities between 50 and 250 mA/cm^2 without changing any other parameters.

[0013] Preferably, the deposition of the active layer is performed by epitaxial Chemical Vapour Deposition.

[0014] Furthermore, the porous semiconductor layer according to the present invention can be a crystalline or amorphous semiconductor material including silicone germanium, III-V materials such as GaAs, InGaAs and semiconducting polymers.

[0015] Advantageously, the foreign substrate comprises a low-cost substrate such as glass, polymeric material.

Short description of the drawings

[0016] Figs. 1 (a) and (b) represent two manufacturing sequences of the prior art for the fabrication of solar cells (PSI process and ELTRAN® process).

[0017] Fig. 2 represents the manufacturing sequence of the present invention for the fabrication of a solar cell.

[0018] Fig. 3 represents the first and the second steps of the manufacturing sequence of the present invention where pore branching results in increased lateral porosity followed by the film separation (lift-off process). This process is described in detail in EP-A-1132952.

[0019] Fig. 4 represents a picture of the free-standing thin film device after peeling and before the transfer to the support.

[0020] Fig. 5 represents the set-up used for the porous semiconductor layer formation according to EP-A-1132952.

[0021] Fig. 6 is representing the dummy substrate to hold the porous semiconductor film during the epitaxial layer deposition.

[0022] Fig.7 represents an adhesived device on a foreign substrate

Detailed description of preferred embodiments

[0023] The widely known silicon on insulator (SOI) technology involves the formation of a monocrystalline semiconductor layer on a insulating material, such as silicon oxide or glass.

[0024] A particular embodiment of the present invention is related to the fabrication of solar cells which are described in details in Figs. 1 and 2.

[0025] The sequence of the prior art process is described in Fig. 1 while Fig. 2 represents the manufacturing process for the fabrication of a solar cell according to the present invention.

[0026] Fig. 1 represents according to the prior art the preparation of a porous silicon layer (double layer 1+2) on a substrate 3 (step 1 in Fig. 1) followed by an epitaxial silicon layer 7 deposition (step 2 in Fig. 1), and the device 6 fabrication of said substrate (step 3 in Fig. 1) and finally the separation of said device from the substrate 3 and the transfer to a foreign substrate 4 in order to possibly re-use the original substrate (step 4 in Fig. 1).

[0027] Fig. 2 is representing the sequence of the method for manufacturing a solar cell according to the present invention. Said method comprises as step 1 the formation of a porous semiconductor layer (double layer 1+2) in the form of a thin-film 10 on an original substrate 3, said formation being immediately followed by the separation of said thin-film 10 by a lift-off process from said original substrate 3 (step 2), the transfer of said thin film 10, and the preparation of the device 6 including epitaxial silicon layer 7 deposition and contact fabrication (step 3). Finally the transfer of the whole device to a foreign substrate 4 in order to realise the solar cell (step 4).

[0028] The lift-off process involving the film separation from its substrate is described in details in Fig. 3.

[0029] The pore formation starts at a certain position, it goes straight down in the semiconductors as shown in Figure 3. When the pores are not deep enough, the reaction occurs at the bottom of the pore. At this time, there are sufficient fluoride ions available at the bottom

but certainly less than the number of fluoride ions available at the surface since they have to diffuse through the pore to the point of reaction. Porosity of the layer increases with decrease in the concentration of HF in solution. Although the initial F-containing solution is not replaced, an in-situ change of concentration is obtained. Therefore, as we go deeper, porosity of the layer increases. The porosity gradient occurs from the point where the availability of the fluoride ion is affected by the diffusion through the pores.

[0030] As pores go sufficiently deep in silicon, the fluoride ion concentration at the point of reaction reduces to a very low level as compared to the surface concentration. This results in the shift of the point of reaction to a slightly higher level because of very high resistance of the lowest part of the pore. This shift in the reaction gives rise to the formation of the branches of the pores. For every dissolution of a silicon atom, one hydrogen molecule results as a product of the electrochemical etching. The hydrogen molecules exert force on the walls of the pores. At some points, because of the branching of pores, the walls become very thin and not able to withstand the hydrodynamic pressure exerted by the hydrogen molecules. This results in horizontal cracks in the layer. The presence of sufficient horizontal cracks results in the separation of the layer from the substrate.

[0031] An example of a free-standing thin film is described in Fig. 4 after the peeling-off and before the transfer to a support.

[0032] The approach of the present invention opens new possibilities in the formation of porous layers in form of thin films by proposing a new sequence for the preparation of free standing thin-film devices to be used for SOI

structures or solar cells in particular. Examples of such porous semiconductor layers called hereunder as PSL could be crystalline and amorphous semiconductor material including silicon, germanium, III-V materials such as Ga As, InGaAs and semiconducting polymers.

[0033] In conventional techniques a double porosity layer is prepared by electrochemical etching and by changing one of the formation parameters such as the electrolytic current density or the HF concentration of the electrolytic solution.

[0034] According to the present invention the parameters of the porous silicon formation remain unchanged and the separation is not reached by changing the current density of the electrochemical solution but by allowing the current to flow for sufficient time.

[0035] An example of a set-up used for the formation of said double porous semiconductor layer has been described in details in Fig. 5.

[0036] Fig. 5 is representing the set-up used for the formation of the porous semiconductor layer (PSL). In such a process, the platinum electrode 8, which is resistant against hydrofluoric acid, acts as a negative electrode. The bottom plate 13 (e.g. stainless steel plate), which is in contact with the silicon wafer 3 (polished side up), acts as a cathode. The rubber ring 12 prevents the outflow of the solution from the contact area of the Teflon® beaker 9 and wafer substrate 3. The rubber ring is kept under pressure by the beaker 9, which in turn is pressurised by a stainless steel threaded ring (not shown).

[0037] According to the process of the present invention, after the preparation of the porous silicon layer, the film obtained is immediately separated from the substrate by a list of processes and then the fabrication

of the device for the solar cell is carried out without permanently transferring the film on other substrates. This makes the process very simple because under these conditions, no worry is justified about the foreign substrate on which the film has to be transferred. At the same time this gives a full freedom of process parameters. Since there is no limitation due to the foreign substrate and due to porosity of the semiconductor layer, any temperature cycle can be used.

[0038] If required, the fabrication of the device itself is performed by transferring the lift-off film 10 to a dummy support 17 in order to realise the epitaxial deposition (see Fig. 6).

[0039] The present invention discloses a very attractive method for the preparation of low-cost, high quality structures, such as SOI structures or solar cells.

[0040] Figure 7 is representing the final structure such as a solar cell whereon the active device 6 has been attached by an adhesive 15 on the low-cost substrate 4.

[0041] According to a preferred embodiment related to the solar cell manufacturing process, the processing is more simple and provides a total freedom in terms of processing parameters, compared to the conventional techniques, e.g. using porous silicon sacrificial layers for thin film transfer processes. The transfer process according to the present invention occurs directly after the preparation of the porous silicon film on a dummy substrate which makes an intermediate layer as in the prior art useless. Such intermediate layers (e.g. hydrogen silsequioxane) require high temperature stability (1100°C) and matching thermal expansion coefficients as well as low impurity contents. For the substrate, similar requirements are necessary. In the opposite, for the process of the present invention, no transfer to the real substrate is

performed and therefore no intermediate layer is used. The handling of the thin layer (film) is the biggest challenge but this difficulty is compensated by fewer constraints due to the reduced number of layers and more freedom in terms of process parameters. The monocrystalline Si thin film solar cells can be attached to any substrate (even flexible substrates) and the handling of this film remains the most critical point.

[0042] The present invention discloses a method able to transfer a thin porous semiconductor film, with a high quality epitaxial layer on the top of said porous semiconductor layer, onto a foreign substrate. The resulting device can be used for the following applications:

- terrestrial solar cells, due to their low-cost,
- space solar cells due to their light weight (thin-film) combined with high efficiency,
- SOI structures due to their high quality of the epitaxial layers.

Description of a preferred embodiment of the invention (solar cells)

[0043] A 20 μm porous silicon film is separated from highly doped P-type, <100> silicon by electrochemical etching in an electrolyte bath containing HF. After annealing of a porous silicon film at 1050°C in H_2, P-type silicon layer with 20 μm thickness is deposited using conventional CVD. In the first trial, a simple two side-contacted solar cell without any photolithography is applied for such free-standing film. An efficiency of 10.6% is achieved for a small area cell (1 cm^2). The other cell parameters are as follows: V_{OC} - 581.3 mV, I_{SC} - 30.29

mA/cm^2 and FF - 60.1 %. IQE analysis reveals that the spectral response of free-standing film with Al backside metallization is significantly increased in the infrared wavelength region as compared to the cell transferred to conventional ceramic substrates.

[0044] The process of the present invention comprises five steps of fabrication:

a) <u>Porous silicon formation and separation from the reusable (original) substrate.</u> (See also EP-A-1132952)

[0045] For all experiments highly boron doped p-type mono-crystalline CZ-Si substrates with a resistivity in the range of 0.02-0.05 Ω-cm and an area of 5x5 cm^2 are used. Porous silicon formation is carried out in a conventional PTFE (Teflon) cell with a silicon sample as anode and a platinum counter electrode as shown in Fig. 1. The electrolyte contained of HF and acetic acid is used. Porous silicon formation is carried out at current density ranging from 50 to 250 mA/cm^2 and HF concentration ranging from 12 to 35 vol % at room temperature under background illumination.

b) <u>Transfer of the porous semiconductor layer to a dummy substrate</u>.

[0046] The porous semiconductor layer is not really attached to the dummy substrate but fixed in between two supports to give mechanical strength to the porous semiconductor layer.

c) <u>Epitaxial silicon layer deposition</u>

[0047] Deposition of active layer is carried out with and without pre-annealing of porous layer in H_2 ambient at 1050°C for 30 min. In first case the aim is to convert the porous silicon into quasi monocrystalline silicone (QMS) which provides a good seeding layer for a CVD layer deposition. An active layer of 10-30 microns is deposited

using dichlorosilane (DCS) or trichlorosilane (TCS) at 1050°C and 1130°C respectively. The porous silicon film is kept (no permanent bonding) between two silicon substrates, with the window on the top substrate for CVD deposition.

d) Device fabrication

[0048] One side contacted and two side contacted solar cell are fabricated while keeping the Porous-Silicon+Epi essentially free-standing (no permanent bonding to any substrate). Efficiency of 10.6% has been achieved on 1 cm^2 area.

e) Attach or transfer solar cell on foreign substrate

[0049] In the final step of fabrication solar cell is transferred to a foreign substrate like Glass, Plastic, etc. using some adhesive.

NOMENCLATURE

1. low porosity semiconductor layer (film)
2. high porosity semiconductor layer
3. compact silicon substrate (reusable / Anode)
4. substrate (dummy)
6. device (epitaxial semiconductor layer with contacts)
7. epitaxial semiconductor layer
8. platinum anode
9. Teflon® beaker
10. thin film
11. solution (HF, …)
12. Viton O-ring
13. back contact
15. adhesive Layer
17. foreign substrate (glass, plastic, etc.-low cost substrate)

CLAIMS

1. A method for manufacturing a semiconductor device, said method comprising at least the following subsequent steps:

- formation of a porous semiconductor layer (1,2) in the form of a thin film (10) on an original substrate (3), said formation being immediately followed by the step of
- separation of said thin film by a lift-off process from said original substrate (3);
- fabrication of a device (6 or 7) on said thin film (10);
- transfer and attachment of said device on a foreign substrate (4).

2. A method as in claim 1, wherein the step of the fabrication of the device comprises the transfer of said thin film to a dummy support (17) whereon the deposition of an active semiconductor layer (7) is performed on said thin film (10), optionally followed by the fabrication of a contacted device on said active semiconductor layer (7).

3. A method as in claim 1 or 2, wherein the lift-off process is achieved by immersing the substrate (3) in a HF solution in concentration between 12 and 35% and using current densities between 50 and 250 mA/cm^2 without changing any other parameters.

4. A method as in claim 2 to 3, wherein the deposition of the active semiconductor layer (7) is performed by epitaxial Chemical Vapour Deposition.

5. A method as in any one of the preceding claims, wherein the porous semiconductor layer (1+2) is a double layer of crystalline or amorphous semiconductor material including silicone germanium, III-V materials such as Ga As, InGaAs and semiconducting polymers.

6. A method as in any one of the preceding claims, wherein the foreign substrate (4) comprises a low-cost substrate.

ABSTRACT

METHOD FOR MAKING THIN FILM DEVICES INTENDED FOR SOLAR CELLS OR SOI APPLICATIONS

The present invention is related to a method for manufacturing a semiconductor device, said method comprising at least the following subsequent steps:

(a) formation of a porous semiconductor layer (1,2) in the form of a thin film (10) on an original substrate (3), said formation being immediately followed by

(b) separation of said thin film by a lift-off process from said original substrate (3);

(c) fabrication of a device (6 or 7) on said thin film (10);

(d) transfer and attachment of said device on a foreign substrate (4).

(Figure 2)

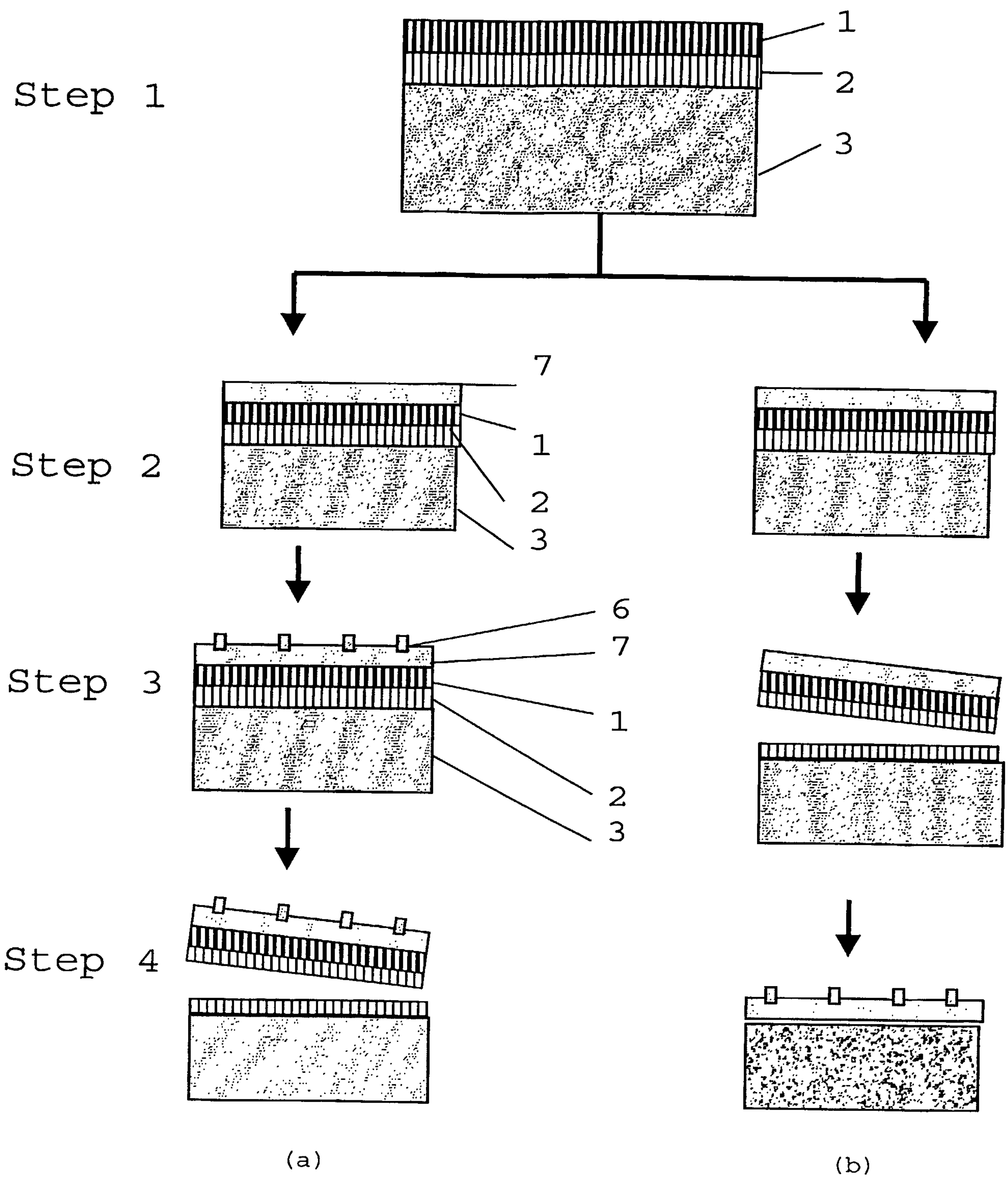

Fig.1

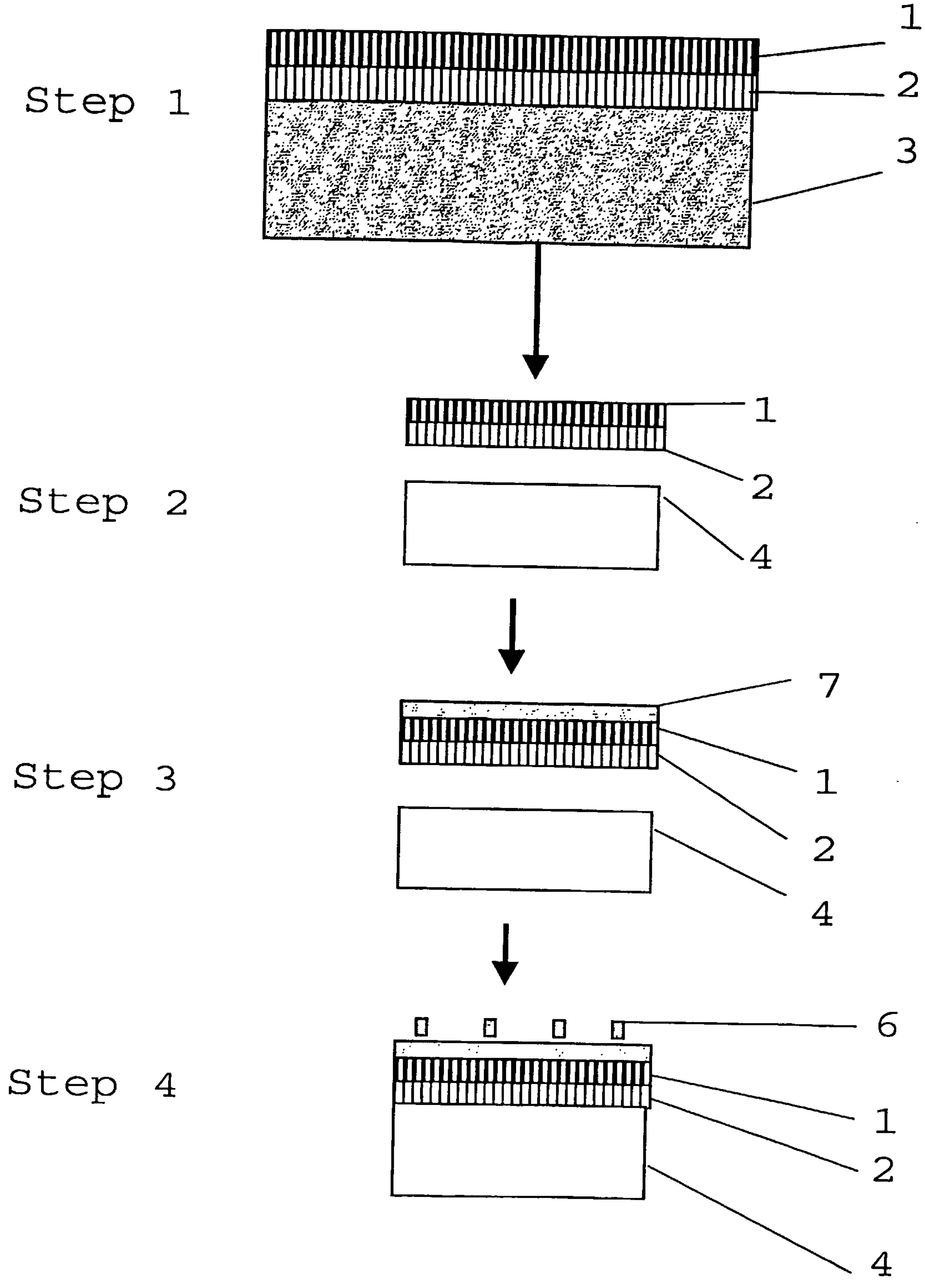

Fig.2

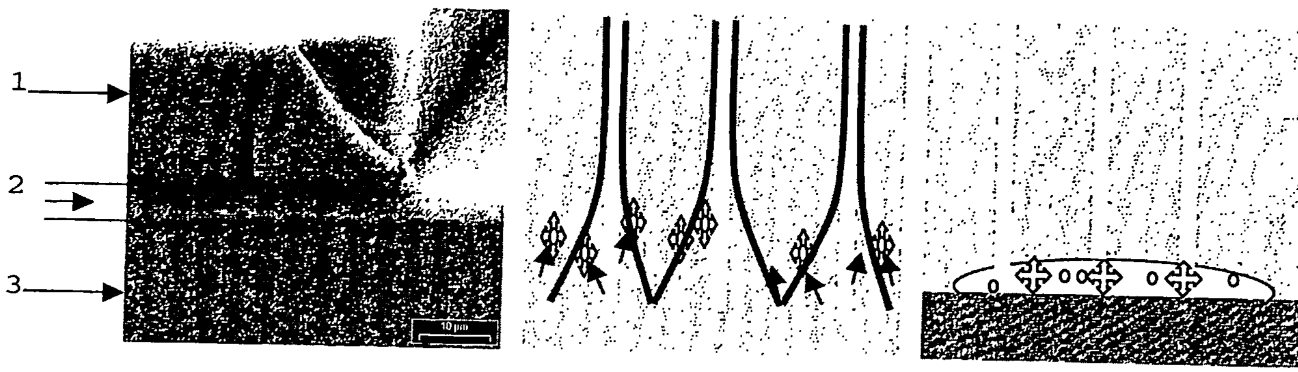

Fig.3

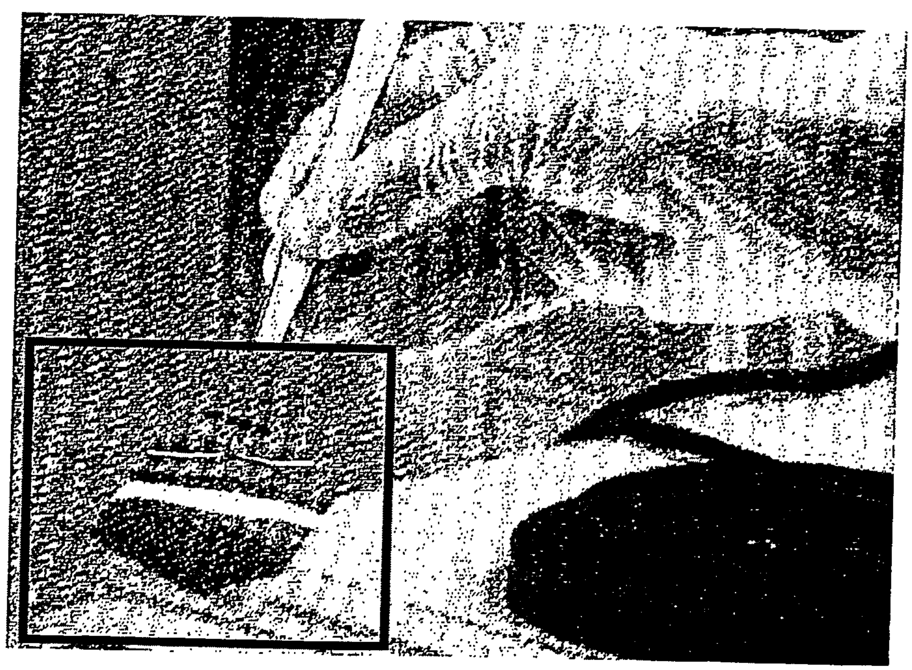

Fig.4

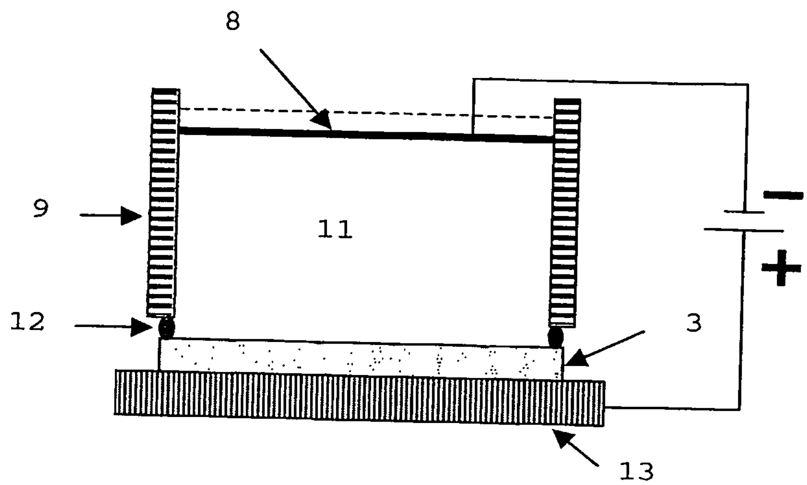

Fig.5

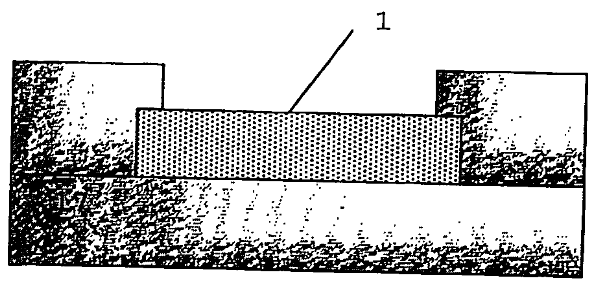

Fig.6

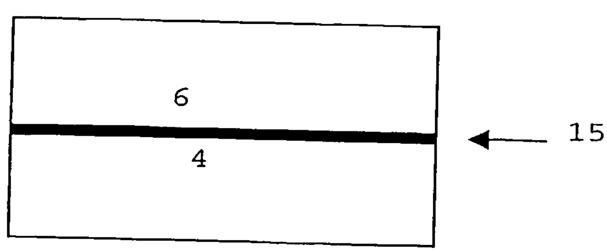

Fig.7